PALM OIL - BASED POLYOL FOR COATINGS

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ABSTRACT

Polyols are widely used in the formulations for polyurethanes. Nowadays, the recent thread of oil price increase has lead government to create the new ideas for polyol production instead of using petroleum. Palm oil (PO) based polyol is an alternative material that may possibly replace petrochemical-based polyol for polyurethane coating material. Polyurethane was synthesized by reacting palm oil-based polyol with isocyanate. The parameters that have been focused throughout this experiment were mol ratio of palm difference weight ratio of hydrogen peroxide for crude palm oil (CPO) to Acetic Acid to H_2O_2 during epoxidation process, reaction time in opening ring and the ratio polyol to isocyante for coating process .The experiment works has been done at UMP's basic engineering laboratory. In this study, PO was first epoxidized to form epoxidation of palm oil (EPO). The process has been carried out with 4 samples at difference weight ratio of hydrogen peroxide (H_2O_2) for CPO to Acetic Acid to H_2O_2 which are 1:5:1, 1:5:2,1:5:4 and 1:5:6.The presence of oxirane ring of EPO was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and the iodine value of EPO was characterized by Potentiometric Titrator. Then, EPO was converted to palm oil-based polyol by the opening ring reaction with ethyl glycol. The process was carried with difference set of reaction time which is 20 minutes, 40 minutes and 60 minutes respectively. The present of hydroxyl group in polyol was characterized by FTIR and acid value was determined by using Potentiometric Titrator. Palm oil-based polyol was mixed with isocyanate to produce polyurethane coating at different ratio polyol to isocyante were 1:1, 1:2 and 1:3. Scanning Electron Microscopy (SEM) is used in order to analyze the surface structure of coating that form. The results shown that lower iodine value (0.85 I_2 g/100g) was obtained by using mol ratio of 1:5:4. At 60 minutes reaction of opening ring showed the present of hydroxyl group at peak 3481 cm^{-1} and the acid value of polyol that obtain at this condition was 3.86 mg KOH. Based on SEM image, by using the ratio polyol to isocyante of 1:3 shows the effect of isocyante on the bubble size and indicate that the bubble size increase with the increase with isocyate content. Based on study, palm oil was able to produce palm oil-based polyol with the low iodine value, low acid value and low functional group which is suitable to be used in coating applications.

ABSTRAK

Polyols digunakan secara meluas dalam rumusan untuk poliliuretana. Pada masa kini, kenaikan harga minyak telah menyebabkan kerajaan untuk mewujudkan idea baru untuk pengeluaran polyol selain daripada petroleum. Polyol bersasaskan minyak sawit merupakan bahan alternatif yang boleh menggantikan polyol berasaskan petrokimia untuk bahan salutan poliuretana. Poliuretana telah disintesis oleh reaksi polyol berasaskan minyak sawit dengan isosianat. Parameter yang diberi tumpuan sepanjang eksperimen ini ialah nisbah mol nisbah berat perbezaan sawit hidrogen peroksida untuk minyak sawit mentah (MSM) kepada Asid asetik untuk H_2O_2 semasa epoxidation proses, masa tindak balas di gelanggang pembukaan dan polyol nisbah untuk isosianat untuk proses salutan . Eksperimen telah dilakukan di makmal kejuruteraan asas UMP. Dalam kajian ini, dimulakan dengan epoxidized proses untuk membentuk epoxidation minyak sawit (EPO). Proses ini telah dijalankan dengan 4 sampel pada nisbah berat perbezaan hidrogen peroksida untuk MSM kepada Asid asetik untuk H_2O_2 yang 1:5:1, 1:5: 2,1:5: 4 dan 1:5:6. Pembentukan cincin oxirane daripada EPO dicirikan oleh Fourier Transform Infrared Spektroskopi(FTIR) dan nilai iodin EPO dicirikan oleh potentiometrik Titrator. Kemudian, EPO telah ditukar polyol berdasarkan minyak sawit oleh cincin reaksi pembukaan dengan etil glikol. Proses ini telah dijalankan dengan perbezaan masa tindak balas iaitu 20, 40 dan 60 minit. Semasa kumpulan hidroksil dalam polyol dicirikan oleh FTIR dan nilai asid telah ditentukan dengan menggunakan potentiometrik Titrator. Polyol berasaskan minyak sawit bercampur dengan isosianat untuk menghasilkan salutan poliuretana pada nisbah polyol berbeza untuk isosianat ialah 1:1,1:2 dan 1:3. Imbasan Elektron Mikroskopi(SEM) digunakan untuk menganalisis struktur permukaan lapisan terbentuk. Keputusan menunjukkan bahawa nilai iodin yang lebih rendah (0.85 I2 g / 100g) telah diperolehi dengan menggunakan nisbah mol 1:5:4. Pada minit ke 60, reaksi pembukaan cincin menunjukkan kumpulan hidroksil terbentuk pada puncak 3481 cm^{-1} dan nilai asid polyol adalah 3.86 mg KOH. Berdasarkan imej SEM, dengan menggunakan polyol nisbah untuk isosianat 1:3 menunjukkan kesan isosianat kepada saiz gelembung .Ia menunjukkan bahawa saiz gelembung bertambah dengan pernambahan kandungan isosianat. Berdasarkan kajian, minyak kelapa mampu menghasilkan polyol berasaskan minyak sawit dengan nilai rendah iodin, nilai asid yang rendah dan kumpulan berfungsi yang rendah adalah sesuai digunakan dalam aplikasi salutan.

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LIST OF ABBREVIATIONS

a	isocyanate mass
b	polyol mass
x	% NCO in isocyanate
y	% OH in polyol

CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
EPO	Epoxidation Palm Oil
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel permeation chromatography
H_2O_2	Hydrogen Peroxide
IV	Iodine number
MPOB	Malaysia Palm Oil Board
MSM	Minyak Sawit Mentah
PO	Palm oil
SEM	Scanning Electron Microscopy
TGs	Triacylglycerol

CHAPTER 1

INTRODUCTION

Polyol is an alcohol with more than two reactive hydroxyl groups. Moreover, polyol also traditionally produced from petroleum. However, production of polyols from petrochemical are costly, non-biodegradable, required more energy and non-environmental friendly (Noor *et al.*, 2013). Polyol is used commonly in food industry and polymer chemistry. Examples of polymeric polyols are polyethylene glycol, polypropylene glycol and many more. These polyols are widely used in formulations for polyurethanes. Example products of polyurethane are thermal insulation, medical implant and many more.

Vegetable oil is an alternative raw material that can be used as raw material of polyol such as soy oil, palm oil, jotropha oil and so on (Sugita *et al.*, 2012). Production of polyol from vegetable oil has more advantage compared with polyol from petrochemical. According to Kiran K.Y. (2005), petroleum is a non-renewable resource and expensive has encouraged researchers to develop new alternatives to petroleum based products from biomass.

In chapter 1, we will discuss about the background of the research which are included raw materials, process and the product that will be produced in this research. In this chapter, we will include the identification of problems, research objectives, research scopes and rational and significance of the study.

1.1 Research Background

Polyurethane is reaction between polyol and isocyante. Moreover, polyurethane also one of the polymer products. Example of polyurethane products is coated, adhesives, foam and many more. Based on research by Sugita *et al.* (2012), world consumption of polyurethane increases every year and an average of 5.1% increase until 2005. Polyol is almost important raw material for making polyurethane. Polyol for polyurethane manufacturing are generally derived from petrochemicals (Tanaka *et al.*, 2008).

Nowadays, the recent trend of oil price increase has lead government to find alternative raw material for polyol production. Palm oil is an alternative raw material that may be used to produce polyols. In Malaysia, Malaysian Palm Oil Board (MPOB) collaborates with Klauditz-Wilhelm-Institute (WKI), Germany has been intensively researched for palm oil-based polyol (Sugita *et al.*, 2012). Figure 1 shows the oil palm tree

Figure 1 The oil palm tree

Oil palm tree consists of three main parts which are trunks, fruit bunches and fronds. The oil palm produced two types of oils. Two types of oils are palm oil from the fibrous mesocarp and lauric oil from palm kernel. According to Teoh C.H. (2002), in the conventional process, fresh fruit bunches are sterilized and stripped of the fruitlets. After that, fresh fruit bunches are digested and pressed at certain pressure to extract oil from fruit bunches called crude palm oil (CPO). Figure 2 shows fresh fruit bunches.

Figure 2 Fresh fruit bunches

To produce palm oil-based polyol, palm oil is first epoxidized to get epoxidation of palm oil (EPO), followed by opening ring with alcohol. The synthesis route is outlined inFigure 3.

Palm Oil

↓ Epoxidation Process

Epoxidation of Palm Oil (EPO)

↓ Ring Opening with alcohol

Palm Oil-Based Polyol

↓ + Isocyanate

Coatings

Figure 3 The Synthesis Route of Coating Process from Palm Oil

Epoxidation of palm oil is done by introducing palm oil through an oxidation process. The epoxidation process is a chemical reaction of converting carbon-carbon double bond to epoxide functional group in vegetable oil, which is a cyclic ether with three ring atom. It is a very import process nowadays because epoxides obtained from vegetable oil can be used as high temperature of raw materials for alcohol or glycols. Research by Carson and Chang (1985), epoxides with higher oxirane values and iodine value are considered to be in better quality.

Then, epoxidation of palm oil (EPO) is introduced to the opening ring process. Research by Hazimah *et al.* (2005), epoxidation of palm oil is reacts with alcohol to produce palm oil based polyol. Examples of alcohol that usually use to react with EPO are glycerol and ethylene glycol.

For the coating Polyurethane, research by Yuan-Chan T.,(2008) , polyurethanes are polymers formed by the reaction of alcohol with two or more reactive hydroxyl functional groups per molecule and isocyanates that have more than one reactive isocyanate group per molecule which is a diisocyanate or polyisocyanate.

1.2 Motivation and Problem Statements

Polyol are currently produced from petroleum. Moreover, the production of polyol from petroleum is expensive due to the trend of oil price increase. According to Kiran K. Y.(2005), the uses of polyol in the USA is approximately 3 billion pounds/year, and worldwide uses of polyol is approximately 10.2 billion pounds/year. Petroleum is non-renewable resources. The lack of petroleum resources and the increase the petroleum price which at a point hit USD 150 per barrel in 2008.Petroleum uses based on monomers in the manufacture of polymers is expected to decline in the coming years because of increasing prices and the high rate of depletion of the stock.

Furthermore, polyol from petroleum is non-environmental friendly. Based on research by Kiran K. Y. (2005), producing 0.45 kg of petroleum based on polyol add 1.6 kg of carbon dioxide to the environment. Then, it was found that polyol from petroleum had potential to higher greenhouse gas emission (Richard and David, 2009). Polyol from petroleum not biodegradable compound. This compound does not have fatty acid and will not support any bacteria. So, it cannot be biodegradable.

1.3 Objective of Research

The objectives of this research are:

1.3.1 To utilize palm oil as an alternative source to produce polyol

1.3.2 To determine the optimum weight ratio for hydrogen peroxide in epoxidation process

1.3.3 To study the effect of reaction time of ethylene glycol in epoxidation of Palm Oil

1.3.4 To investigate the effect of isocyanate on polyol for coating

1.4 Scope of Research

In order to achieve the objective, the following scopes have been identified and to be applied:

1.4.1 The effect of hydrogen peroxide in epoxidation process

1.4.2 The effect of ethylene glycol in polyol synthesis

1.4.3 The effect of isocyanate in coating process

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

In Chapter two divide into three parts which is raw material, process production and product. The raw material that used in this research was palm oil. Process production that included in this research ware epoxidation and opening ring process. The product for this research were polyol and polyurethane. Moreover, the related process descibtion , principle and application of the parts were included in this chapter.

Chapter three explains the material and methodology used to achieve the research objectives .It starts with the epoxidation of palm oil (EPO). Then, the synthesis of EPO to polyol by opening ring reaction. The last method was preparation of polyurethane coating. The characterization of the sample was done after finish one process.

In chapter four, results of the present work are presented and discussed. The optimised parameters are compared with the parameters reported in the literature. The experimental results include the wave numbers of EPO and palm oil-based polyol, iodine value of EPO, acid number of palm oil-based polyol and morphology of polyurethane coating were discussed based on the reaction theory and literature.

Conclusions of the present work and relevant recommendations for future work are given in chapter five.

CHAPTER 2

LITERATURE RIVIEW

In this chapter, the finding of related articles from MPOB website and I-portal is needed in order to do a literature review. The literature review is research done in the past by other people and it is needed to support our research objectives.

2.1 History, Habitat, Tree and Industrial Development of Oil Palm

The oil palm or Elaeis guineesis Jac is a tropical palm tree. The oil palm tree is a tropical palm tree under the family of palm originally come from Guinea; West Africa (Yusof, 2000) is originally illustrated by Nicholas Jacquin in the year of 1763. Oil palm was introduced to Malaysia in 1910 by Scotsman William Sime. Sime Darby and Boustead who are the first plantations British plantation owner were established and operated in Malaysia.

Furthermore, the most suitable culture for oil palm is soil must be free from draining with low pH, but does not thrive at very high pH, which is greater than 7.5. Oil palm culture is done in low altitude less than 500m above sea level with 15 ˚ from the equator in the humid tropics. The soil is properly drained with evenly distributed rainfall of 1,800 to 2,000 mm/year, but will tolerate rainfall up to 5,000 mm/year. If there are more than three consecutive months with less than 100 mm rainfall per month, potential yield will be reduced and oil palm is sensitive to poor drainage and drought.

Oil palm tree consists of three main which are trunks, fruit bunches and fronds. The height of oil palm tree usually with an unbranched tree from 20 m to 30 m and its trunk is formed over 3 years old when the apex has reached its full diameter the form of an inverted cone after intermodal elongation take place. The weight of bunches of fruit is about 10 kg to 25 kg and sometime might be up to 50 kg. Moreover, the most suitable time to harvest ripe fruits is 5 to 6 months after flowering. A bunch of fruit can produce 500 until 4000 number of fruit. The fruit is reddish with ovoid type shaped, have 2 cm to 5 cm measurement of length and weight scale from 3 g to 30 g. Each of the fruit contains a single seed surrounded by a soft oily pulp. The palm oil produces two types of main vegetable oil. The examples of vegetable oil or palm oil extracted from the mesocarp of the fruit and palm kernel oil extracted from the seed.

Oil palm tree was first introduced to Malaysia in year 1870.According to Official Palm Oil Information Source, 1.5 million hectares were planted with oil palm tree and the amount of palm oil plant in Malaysia had increased to 4.3 million hectares in year 2007.The total planted area with oil palm tree in Malaysia was 4.917 million hectares until year 2011.Figure 4 shows the planted area of oil palm tree in Malaysia from year 1975 until year 2011.Furthermore, Malaysia now is the second larger producer of palm oil in the world after Indonesia in year 2006.

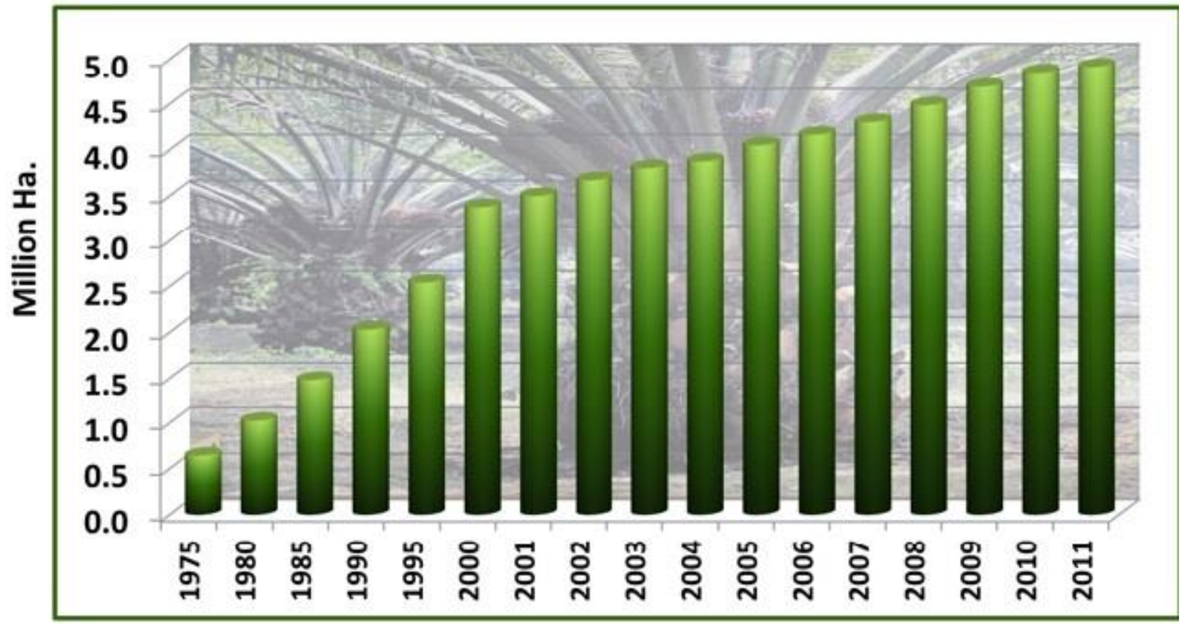

Figure 4 The Planted Area of Oil Palm Tree in Malaysia from year 1975 until year 2011

2.2 Palm Oil

2.2.1 Characteristic of Palm Oil

There are two types of oil, which is palm oil from fibrous mesocarp and lauric oil from palm kernel. Fresh fruit bunches are sterilized and stripped of the fruits. After that, it will digest and pressed to extract the crude palm oil (CPO). The nuts are separated from fibre to obtain crude palm kernel oil (CPKO). Palm kernel cake is the byproduct of fresh fruit bunches.

Then, fractionation of CPO and CPKO in the refinery produces the liquid stearin fraction and solid stearin component. Palm oil has a balanced ratio of saturated and unsaturated fatty acids. Moreover, palm kernel oil has mainly saturated fatty acid, which is similar to the composition of coconut oil. According to Salmiah A. (2000), palm oil has a higher amount of saturated fatty acid, but it is more stable and less prone to oxidation at high temperature compare to soy oil. The composition of fatty acid is compared with coconut oil and soy oil in Table 1. These are shown in Table 1, table of fatty acid compositions of palm oil products, soy oil and coconut oil.

Table 1 Fatty acid compositions of palm oil products, soy oil and coconut oil

Fatty Acids	Weight Percentage						
	Palm Oil	Palm Olein	Palm Stearin	Palm Kernel Oil	Palm Kernel Olein	Coconut Oil	Soy Oil
C6:0				0.3	0.4	0.2	
C8:0				4.4	5.4	8.0	
C10:0				3.7	3.9	7.0	
C12:0	0.2	0.2	0.3	48.3	41.5	48.2	
C14:0	1.1	1.0	1.3	15.6	11.8	18.0	
C16:0	44.0	39.8	55.0	7.8	8.4	8.5	6.5
C18:0	4.5	4.4	5.1	2.0	2.4	2.3	4.2
C18:1	39.2	42.5	29.5	15.1	22.8	5.7	28.0
C18:2	10.1	11.2	7.4	2.y	3.3	2.1	52.6
Others	0.8	0.9	0.7	0.1	0.1		8.0
Iodine Value	53.3	58.4	35.5	17.8	25.5	9.5	133.0

Source :Salmiah Ahmad,2000

2.2.2 Chemical Composition of Palm Oil

The major constituents of palm oil are triacylglycerols (TGs). Over 95% of palm oil consists of TGs which is glycerol molecules and each of it contain esterified with three fatty acid components. Research by Kalyana S.P.(2002), during the oil extraction the hydrophobic of TGS attract to other fat or oil soluble cellular components. Furthermore, there is the minor component in palm oil, which are phosphatides, strerols, pigments and many more. Moreover, in palm oil also have metabolites components that act in biosynthesis of TGs and products from lipolytic activities. Example of metabolites component are monoglycerols (MGs) , diglycerols (DGs) and last but not least free fatty acid (FFAs).

The fatty acids are any class of aliphatic acids that contain in animal, vegetable fats and oil. In palm oil, the major of fatty acid are myristic (14:0), palmitic, stearic, oleic and linoleic (18:2). Table 2 shows the typical fatty acid composition (%) of palm oil in Malaysia.

Table 2 Typical Fatty Acids Composition (%) of Palm Oil in Malaysia

Fatty acid chain length	Mean	Range observed	Standard deviation
12:0	0.3	0-1	0.12
14:0	1.1	0.9-1.5	0.08
16:0	43.5	39.2-45.8	0.95
16:1	0.2	0-0.4	0.05
18:0	4.3	3.7-5.1	0.18
18:1	39.8	37.4-44.1	0.94
18:2	10.2	8.7-12.5	0.56
18:3	0.3	0-0.6	0.07
20:0	0.2	0-0.4	0.16

Source :Kalyana Sundaram PHD,2002

Palm oil is used in edible and non-edible applications. Research by Kalyana S.P.(2002), almost ninety percent of the world palm oil production is used as edible purposes. The remaining ten percent of palm oil is used for non-edible applications such as in soap and oleo chemical industries. For use on edible and non-edible, palm oil is normally refined (Sarmizi *et al*., 2009). In food industries refined palm oil is used as margarine, deep frying fat and specialty fats.

Moreover, palm oil and palm oil kernel are now used commercially in ice cream production to replace butterfat. This is because palm oil is more economical than other oils and also easily available. Furthermore, palm oil is more stable to oxidation than butterfat. Research by Malaysian Palm Oil Council, palm oil is an attractive ingredient in food industries because it contains a high proportion of higher melting triglycerides. For shortening manufacturing, palm oil combines with palm stearin and blend with liquid oils. In addition, the quantity of palm oil in shortening usually from thirty to forty percent. Palm shortenings are used widely in baking industry. Figure 5 shows the uses in food application of palm oil.

Figure 5 The Uses in Food Application of Palm Oil

The important future application of palm oil in food industry is the use of refined red palm oil in cooking (Sarmizi *et al*., 2009). Refined red palm oil contains nutritious oil rich in vitamin E and β-carotene. The functions of β-carotene are antioxidant and inhibitor effect in colon cancer cell.

Then, for the non-edible uses of palm oil include the production of soap, polyols epoxidized palm oil, polyurethane, cosmetics, oleochemical and many more. According to Malaysian Palm Oil Council, production of soap is one of the most important applications of oils and fats. Coconut oil and tallow have been traditionally used in soap production. Nowadays, palm oil and palm kernel oil offer good and competitive alternatives respectively as raw material for soap making.

2.3 *Epoxidation Process*

2.3.1 *Principle of Epoxidation Process*

Epoxidation a chemical reaction of converting carbon-carbon double bond to epoxide function group which is consists of three member ring with two carbon atoms and one oxygen atom.According to Saurabh *et al*.(2011), double bonds in vegetable oils are used as reactive sites in coating and they also acts as epoxidation.Moreover, epoxidation is widely known as function of double bonds in vegetable oils as introduces epoxy group or oxirane oxygen at located double bonds (Syafiq *et al*., 2013). Figure 6 shows the epoxidized with carbon-carbon double bond being converted into oxirane ring.

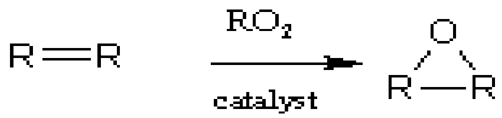

Figure 6 The Epoxidized with Carbon-Carbon Double Bond being converted into Oxirane Ring

Research by Saurabh *et al.* (2011), epoxidized oil contains the epoxide group or oxirane ring which consists of three elements in epoxide ring.There are a few established process of epoxidation which are

- Epoxidation by conventional method
- Epoxidation using acid ion exchange resin
- Epoxidation using an enzyme

Epoxidation by Conventional method

This method is commonly used in the process of epoxidation. Epoxidation process are usually carried out by reacting a carboxylic acid with concentrated hydrogen peroxide or known as peroxides formed in-situ. Moreover, this process is currently used in large scale by industry.

Kinetics epoxidation of cottonseed oil was done using hydrogen peroxide catalyzed by liquid inorganic acids (Dinda *et al*., 2008). They used formic acid as an oxygen carrier, but when they further their research they found that acetic acid is more effective oxygen carrier. Hydrogen peroxide act as oxygen donor and acetic acid acts as an oxygen carrier in the presence of catalytic in organic acid (Saurabh *et al*.,2011).Research by Dinda *et al*. (2008), sulphuric acid was found as the most efficient and effective catalyst out of all inorganic acid. Moreover, when the higher temperature and acid concentration it will reduce the reaction time needed to reach the maximum conversion of oxirane value. However, it will simultaneously increase the extent of oxirane ring cleavage to glycols (Patil and Waghmare, 2013).

Similarly, kinetics of in-situ epoxidation of soybean oil, sunflower oil and corn oil by using peroxyacetic acid with sulphuric acid as catalyst. Among all this, soybean has the greatest conversion rate and lower the activation energy for epoxidation by using peroxyacetic acid (Cai *et al*., 2008).

Epoxidation using organic and inorganic peroxide are suitable for clean and efficient epoxidation for vegetable oil. Research by Campanella *et al*. (2004), epoxidation by using organic and inorganic peroxide can be rendered cleaner by using heterogeneous catalysts instead of using traditional homogeneous catalyst.